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(54) **Printing of fabrics**

Bedrucken von Textilmaterialien

Impression de matériaux textiles

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Printed by Jouve, 75001 PARIS (FR)

Description

This invention relates to the printing of fabrics.

There are many occasions in which it is desired to produce a pattern or design on fabrics other than by weaving or knitting a pattern or design into them by using threads of different colours. The method by which this aim is most often achieved is by the use of a printing process of one kind or another.

An important type of textile printing is known as discharge printing in which a dyed fabric is printed with a suitable printing ink which contains chemicals capable of destroying the ground colour of the fabric during heating or steaming treatment. The fabric is then washed off to remove undesirable residues and to give a coloured fabric with a design of substantially uncoloured material. In an important variant of this process, the printing ink contains colouring matters which are resistant to the chemical degradation process of discharging and which are fixed to the fabric during the heating treatments which are involved. In this way, so-called "illuminated" discharge prints may be produced using vat dyes or resin bonded pigments as colouring matters. Even though the colouring matters used for the production of illuminated discharge prints may normally be fixed to the fabric, generally cotton or some other cellulosic or substantially cellulosic material, by coloration processes which do not require washing off, when the colouring matters are used in discharge printing, a washing off stage is involved due to the need to remove the residues of the chemicals involved in the discharge processes.

Discharge pigment printing processes have been described in which a fabric, dyed with a dye or a mixture of dyes susceptible to chemical degradation to produce colourless or virtually colourless products, is printed with an ink containing a discharge agent, finely dispersed pigments in an aqueous medium, a resin binder capable of polymerising to bond the pigment particles to the fabric, and various catalysts etc. to enhance the reactions. The fabric is dried and then steamed for a period of minutes to produce the discharge. The fabric is then baked to polymerise the resin binder and washed off to remove undesirable residues.

EP-A-0036252 discloses a process of decorating dyed fabric, which comprises the steps of: applying a printing paste, containing at least one reagent capable of reacting with the dye in the fabric at least substantially to destroy its colour, and agents assisting the colour-destroying reaction, water and humectant, to desired image areas forming a design on the fabric, and subjecting the fabric with the applied paste to a heat treatment prior to drying the fabric to fix the design in the fabric. In the specific process described, a separate paste is also applied to the fabric before or after the other printing paste just noted, which contains a dyestuff. The first printing paste prevents some of the dye in the second paste from becoming fixed to the fabric. This process makes washing of the fabric being treated necessary, in order to remove such dye as has been prevented from fixing, before the effects of the process are visible.

It is known that heat treatments of fabrics required in many textile printing processes can be done more favourably between a pair of impermeable layers, as is disclosed in FR-A-1167740.

A serious disadvantage of these normal procedures of discharge printing is that the results of the process are not apparent for some time, i.e. until after the heat treatment and washing off processes have been completed. This means that the printer is unable to correct faults during the run of the print and the printed fabric is subject to accidental damage due to, say, unusually damp atmospheres while it is waiting in the factory for the next process. For this reason, discharge printing is subject to a high percentage of rejects as compared with other printing methods in the textile industry.

The need to wash off the fabrics is a further disadvantage of existing methods of discharge printing. Washing off creates undesirable effluent requiring processing before disposal and increases production costs due to the expense of drying. Many textile print works are precluded from producing discharge prints because the necessary washing and drying equipment is not available.

Despite these disadvantages, discharge prints have been successfully produced for many years on fabrics in a continuous web. However, discharge printing has not been used for decorating garments, or garment panels from which garments are to be made, because textile materials in such a form cannot be washed off without creating expense as well as inconvenience in later processing. Any decoration process used for such materials thus has to be substantially dry, and various dry processes have indeed been developed for textile printing. A further reason for avoiding wet processing garments or garment panels is that it is essential to maintain the dimensional stability of the material in order to control either the garment size or the fit of the decorated panels with other non-decorated panels in making up the garment. Thus, the opportunities offered by discharge printing have, until now, been wholly unavailable to the printer of garments and garment panels.

We have now found that, by using certain print formulations, and a two-stage heat treatment process, improved fabric prints may be obtained. If the print formulation is a discharge print formulation, all the above disadvantages and limitations of discharge printing may be avoided, and printing may be carried out on continuous lengths of fabric, garments or garment panels using those formulations and subjecting the print to appropriate dry heat treatment processes. Discharge prints can be obtained without any need for wet processing at any stage after the application of the printing ink and with the discharge effect fully apparent within a very short time after printing.

It is observed that throughout this specification the term "colouring materials" is used to indicate a pigment or a

dyestuff or a mixture of both which will give a coloured effect, and the term is used to include both black and white, as well as spectral colours.

According to the present invention, there is provided a process of decorating dyed fabrics as described above which is characterised in that the printing paste contains at least 8% by weight of a humectant; and wherein the heat treatment includes maintaining the fabric at a temperature higher than 100°C for a period during which the fabric is confined between a pair of layers of impermeable material.

The fabric may then be subjected to a second heat treatment, the conditions of which are designed to fix any colouring materials in the printing paste to the fabric to give a fast to washing result. Alternatively, discharge printed or decolorised areas may be overprinted with colouring material to produce a design in a second printing step.

The paste needs to contain at least one reagent capable of reacting with the dye in the fabric at least substantially to destroy its colour (i.e. a discharge agent) together with agents assisting the reaction such as acids, alkalis, reduction catalysts and the like.

Preferably, during the first heat treatment, or part thereof, the fabric is subject to pressure, e.g. by being passed through a roller nip while being confined between two impermeable layers or by being held between two heated plates coated with impermeable material for an appropriate period of time.

The first heat treatment referred to above needs to be carried out for only a relatively short period of time and, immediately thereafter, the discharge process is complete. Thus, the printer may judge more accurately, and at an early stage in the printing operating, whether the print is satisfactory. The exact time necessary for the first heat treatment stage will vary with the fabric, the quantity of discharge ink applied and the nature of the dyestuff applied to the fabric and which it is necessary to discharge, but using appropriate temperatures and apparatus it can be as low as 10 seconds. Usually 20 to 30 seconds is convenient, though longer treatment times, e.g. up to 60 seconds, can be used if desired.

It is important to subject the fabric to the heat treatment before the print on it has dried. Because of the high concentration of humectant in the printing paste, however, the heat treatment does not have to be carried out immediately and a delay between printing and heating of more than a minute can, under appropriate circumstances, be allowed without detriment. The heat treatment should, however, be carried out before the print paste has materially dried out on the fabric.

A variety of humectants may be used of which the following are particularly suitable:

Urea
Glycerol
Polyethylene Glycols
Thiodiglycol
Ethoxylated esters

Such humectants are known to be used in textile printing to prevent inks drying on the silk screens used in printing. Normally for this purpose they are present in relatively low concentration in the printing ink, i.e. 3-4%. In the inks of the present invention they are required to constitute at least 8-9% of the ink formulation, preferably 12-15%.

A particular advantage of the printing process of the present invention is the soft handle conferred by the heat treatment especially when the ink incorporates pigments and binders to produce a coloured discharge.

The precise mechanism by which the improvements in discharge printing processes which can be obtained using the method of the present invention are achieved is not known. It is thought that during the heat treatment, while the temperature of the fabric is raised to more than 100°C under light pressure, the superheated steam atmosphere that results causes the discharging agent or agents present to react vigorously and completely with the dye on the fabric leading to the destruction of the chromophoric system and, when suitable dyes are selected for the dyeing, the production of substantially uncoloured products. The role of the humectant during this process is thought to be to extend the time during which the fabric is effectively moist beyond that which would apply if it were not present, thus allowing a longer and more useful reaction time and ensuring that the reactions are complete during the short treatment time involved. A further benefit which is observed when the pigments and pigment binders are incorporated into the printing ink is that excellent penetration and a soft handle are obtained due, it is believed, to the combined assistance to penetration given by the humectant and the superheated steam.

In one form of the present invention, the printing ink incorporates a pigment or a mixture of pigments which are chemically stable to the discharge agent and a pigment binder or mixture of binders together with any desired catalysts which will promote the curing of the binder or binders in a second heat treatment following the first discharging heat treatment. Agents enhancing softness of handle or any other desired effect may also be included as required. Suitable pigment binders are well known in the general field of pigment printing textiles but due to the special conditions associated with the production of the colour discharge, not all of the binders which are used under normal circumstances will give a fully satisfactory result due to discolouration or other degradation reactions which may occur. The printer should therefore select suitable binder by experiment.

Another kind of pigment dispersion which may be used in this form of the invention is that known as water based on water compatible plastisol inks. These may be mixed with the discharge agent and the humectant and printed in the usual way. The fabric is then heat treated to produce the discharge effect using heating between impermeable blankets as described. Due to the thermoplasticity of plastisol inks, it can be advantageous to cover the print with a sheet of release paper to prevent adhesion to the impermeable blankets during this stage of the process. After the discharge is complete, the print is fully cured by passage through a hot oven in the usual way for such inks. This procedure offers considerable advantage over the simple application of these inks on to dyed materials since discharging the colour makes it unnecessary to have sufficient ink present to mask the ground shade and consequently softer, better defined prints with a more attractive handle can be obtained.

A special advantage of the present invention is the rapidity with which the full discharge effect becomes apparent. This enables the discharged area of a final print to be produced in the course of a sequence of application of different inks to the fabric to produce a final design. Thus, the whole area to be decorated may be printed with a colourless binder free discharge ink constituted in accordance with the present invention and the printed fabric heated between to hot plates for a short period or a succession of short periods, e.g. two times 5 seconds at 160°C. The discharge printed area may then be printed with a variety of white or coloured inks without the requirement that the colouring matters be stable to the discharge reaction. It is thus possible to combine discharge printing with the application of reactive dyes in a way which cannot be achieved except with very considerable inconvenience by conventional discharge printing because of the time lag noted above between printing and the production of the discharge. Similarly, pigments may be selected when this form of the invention is employed which are unstable to discharging. So-called expanding inks which increase in volume on heating may also be employed as well as adhesives for the subsequent application of metallic or other decorative effects to the fabric. This variant is of particular value in the printing of both regular and water based plastisol inks on to coloured grounds since the discharge removes the need to apply sufficient ink to mask the ground colour so the less ink can be applied with consequent better design definition, economy and handle. The following Examples will serve to illustrate the invention.

Example 1

A printing ink is prepared containing the following (% by weight):

Imperon Binder 506	10.6%
Alcoprint PHL	17.6%
Water	45.5%
Titanium Dioxide (as a 50% aqueous dispersion)	13.6%
Diammonium Hydrogen Phosphate	3.3%
Viscalex HV30	2.8%
Zinc Formaldehyde Sulphoxylate	6.6%

Imperon Binder 506 is an aqueous emulsion of acrylic polymers manufactured by Hoechst UK Ltd.

Alcoprint PHL is a mixture of organic salts and ethoxylated esters manufactured by Allied Colloids Ltd.

Viscalex HV30 is a mixture of polyacrylic acid derivatives manufactured by Allied Colloids Ltd.

Using this ink, a design is printed by silk screen on to a cotton fabric dyed to a full red shade using Remazol Brilliant Red F3B (Hoechst UK Ltd). The printed fabric is then passed into a hot oven at 180°C between two continuous impermeable blankets held together to prevent drying for 30 seconds. The blankets are so arranged that, before emerging from the oven, the fabric passes between pressure rollers. It can be seen that, as the fabric emerges from the oven, the red dye is discharged in the printed areas to give a white design. The fabric is then passed through a hot oven at 180°C for 1 minute to complete polymerisation of the binder and fixation of the white pigment. The design produced in this manner is fast to washing at 60°C, to wet or dry rubbing and to light.

If the printing is repeated without the use of the impermeable blanket, it is found that the discharge effect is only partially produced, is not stable to light, and the printed fabric has much harsher less desirable handle.

Example 2

A printing ink is prepared containing the following (% by weight):

Acramine Binder SLN	11.1%

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(continued)

Glycerol	19.1%
Titanium Dioxide (as a 50% aqueous dispersion)	13.1%
Copper Phthalocyanine as an aqueous dispersion)	5.0%
Water	34.4%
Isopropanolamine	3.5%
Viscalex V30	6.8%
Formamidine Sulphinic Acid	7.0%

Acramine Binder SLN is an aqueous emulsion of acrylic polymers manufactured by Bayer.

Using this ink, a design is printed by silk screen on to a cotton fabric dyed to a yellow shade by the pad-batch (cold) process using Remazol Brilliant Yellow 4GL (Hoechst UK Ltd). The printed fabric is then heated for 25 seconds in a book press at 175°C between impermeable felts. On removal of the fabric from the press, it is seen that it is printed with a bright blue design on a yellow ground. The fabric is then passed through a hot oven for 2 minutes at 185°C to complete fixation of the white and blue pigments. The design produced in this way is fast to washing at 60°C, to wet and dry rubbing and to light. It possesses a soft attractive handle.

Example 3

A printing ink is prepared containing the following (% by weight):

Hydroxymethyl cellulose	5.0%
Alcoprint PHL	12.5%
Monoethanolamine	3.5%
Formamidine Sulphinic Acid	7.0%
Water	72.0%

A cotton garment panel dyed to a violet shade with Remazol Violet 5R (Hoechst UK Ltd) is mounted on a carrier board in a multicolour screen printing unit and printed with a design using the above ink. The mounted panel is then moved to the second station on the machine where it is pressed between heated plates at 165°C for 5 seconds. It is then moved to the third station where it is pressed between plates as before. At this point, it can be seen that the panel has a white discharged design in the printed areas.

Printing may then be continued using the fourth and subsequent printing stations to apply any desired coloured ink containing dyes or pigments as required. These may be fixed by any appropriate method to produce their normal fastness but with their normal shade due to their having been printed on a white ground as results of the discharge produced.

Claims

1. A process of decorating dyed fabric, which comprises the steps of: applying a printing paste, containing at least one reagent capable of reacting with the dye in the fabric at least substantially to destroy its colour, and agents assisting the colour-destroying reaction, water and humectant, to desired image areas forming a design on the fabric, and subjecting the fabric with the applied paste to a heat treatment prior to drying the fabric to fix the design in the fabric, characterised in that the printing paste contains at least 8% by weight of a humectant; and wherein the heat treatment includes maintaining the fabric at a temperature higher than 100°C for a period during which the fabric is confined between a pair of layers of impermeable material.

2. A process as claimed in Claim 1, wherein the printing paste contains colouring materials and means for fixing the colouring materials in the fabric, and wherein the process comprises a further treatment step under conditions of time and temperature adapted to fix such colouring materials in the fabric to render them wash fast.

3. A process as claimed in Claim 1 or 2, wherein, subsequent to the application of the printing paste and heat treatment step(s), the fabric is overprinted with a colouring material to produce a design in a second printing step.

4. A process as claimed in any preceding claim, wherein the printing paste contains at least 12% by weight humectant.

5. A process as claimed in any preceding claim, wherein the humectant is one or more of urea, glycerol, polyethylene glycol, thiodiglycol and ethoxylated esters.

6. A process as claimed in any preceding claim, wherein the printing paste contains plastisol ink components, and wherein the printed face of the fabric is covered during the heat treatment step(s) with a release paper.

Patentansprüche

1. Verfahren zum Dekorieren von gefärbtem Gewebe, das folgende Schritte umfaßt: Aufbringen einer Druckpaste, enthaltend mindestens ein Reaktionsmittel, das mit dem Farbstoff in dem Gewebe reagieren kann, um dessen Farbe zumindest im wesentlichen zu zerstören, und Mittel, die bei der Farbzerstörungsreaktion helfen, Wasser und Feuchthaltemittel, auf die gewünschten Bildbereiche, die auf dem Gewebe ein Muster bilden, und Wärmebehandeln des Gewebes mit der aufgebrachten Paste, bevor das Gewebe getrocknet wird, um das Muster in dem Gewebe zu fixieren, dadurch gekennzeichnet, daß die Druckpaste mindestens 8 Gew.-% eines Feuchthaltemittels enthält, und daß das Gewebe bei der Wärmebehandlung auf einer Temperatur von über 100°C gehalten wird, und zwar für eine Zeitdauer, während der das Gewebe zwischen zwei Lagen undurchlässigen Materials eingeschlossen ist.

2. Verfahren gemäß Anspruch 1, worin die Druckpaste Farbmittel und Mittel zum Fixieren der Farbmittel in dem Gewebe enthält, und worin das Verfahren einen weiteren Behandlungsschritt unter solchen Zeit- und Temperaturbedingungen umfaßt, daß die Farbmittel in dem Gewebe so fixiert werden, daß sie waschfest werden.

3. Verfahren nach Anspruch 1 oder 2, worin nach der Aufbringung der Druckpaste und dem (den) Wärmebehandlungsschritt(en) das Gewebe mit einem Farbmittel überdruckt wird, um ein Muster in einem zweiten Druckschritt zu erzeugen.

4. Verfahren nach einem der vorstehenden Ansprüche, worin die Druckpaste mindestens 12 Gew.-% Feuchthaltemittel enthält.

5. Verfahren nach einem der vorstehenden Ansprüche, worin das Feuchthaltemittel einen oder mehrere der Stoffe Harnstoff, Glycerin, Polyethylenglycol, Thiodiglycol und ethoxylierte Ester enthält.

6. Verfahren nach einem der vorstehenden Ansprüche, worin die Druckpaste Plastisoldruckfarbenkomponenten enthält und worin die bedruckte Seite des Gewebes während des Wärmebehandlungschrittes (der Wärmebehandlungsschritte) mit einem Trennpapier abgedeckt ist.

Revendications

1. Procédé pour décorer un tissu teint, comprenant les étapes consistant à : appliquer une pâte d'impression, contenir au moins un réactif capable de réagir avec la teinte du tissu au moins sensiblement pour détruire sa couleur, et aider les agents dans la réaction destructrice de couleur, de l'eau et d'agent humectant, sur des zones d'image désirées formant un dessin sur le tissu, et soumettre le tissu avec la pâte appliquée à un traitement à la chaleur avant de sécher le tissu pour fixer le dessin sur le tissu, caractérisé en ce que la pâte d'impression contient au moins 8 % en poids d'un agent humectant ; et dans lequel le traitement à la chaleur comprend le maintien du tissu à une température supérieure à 100°C pendant une durée au cours de laquelle le tissu est confiné entre deux couches de matière imperméable.

2. Procédé selon la revendication 1, dans lequel la pâte d'impression contient des matières colorantes et des moyens pour fixer les matières colorantes dans le tissu, et dans lequel le procédé comprend en outre une étape de traitement supplémentaire dans des conditions de temps et de température adaptées pour fixer ces matières colorantes sur le tissu afin de rendre leur rinçage rapide.

3. Procédé selon la revendication 1 ou 2, dans lequel, consécutivement à l'application de la pâte d'impression et des étapes de traitement à la chaleur, le tissu est surimprimé à l'aide d'une matière colorante pour produire un dessin dans une seconde étape d'impression.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel la pâte d'impression contient au moins

12 % en poids d'agent humectant.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'agent humectant est un élément ou plus du groupe constitué de l'urée, du glycérol, du polyéthylèneglycol, du thiodiglycol et des esters éthoxyliques.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel la pâte d'impression contient des éléments d'encre en plastisol, et dans lequel la face imprimée du tissu est recouverte au cours de l'étape, ou des étapes, de traitement à la chaleur à l'aide d'un papier couché anti-adhésif.